A FUNDAMENTAL STUDY OF CRYSTALLINE AND GLASSY PHASES IN VITRIFIED WHITEWARE BODIES

BY

MILTON ALFRED TUTTLE

B.S., Alfred University, 1941

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AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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The ceramic industry manufactures products by the application of heat to raw materials containing silica or silicates as essential ingredients. The three major raw materials of conventional whiteware bodies are clay, feldspar and silica. These materials form the groundwork upon which the blending variations are carried out with minor additions of other ingredients. Since the clay, feldspar and silica are natural occurring minerals, they contain accessory minerals which introduce such additional oxides as lime, magnesia, titanium dioxide and ferric oxide. A complex number of constituent oxides comprises the chemical composition of the typical whiteware body.

The application of heat to the raw whiteware body brings about changes in chemical, physical and mineralogical compositions. A succession of dissociation, reaction, solution, crystallization and recrystallization occurs during the heating and cooling periods. The complete dissociation of the raw materials into constituent oxides takes place over a wide range of temperatures. The oxides formed by dissociation processes react with each other and any undissociated material present to form new crystalline phases, solid phase combinations and more commonly a melt. The melt forms a glassy matrix upon subsequent cooling. During the vitrification process, the amount and composition of the crystalline and glassy phases depends upon the composition of the raw materials, the firing temperature and the heat treatment. These factors influence the temperature of melt formation, rate of solution of quartz, and type and amount of new crystalline phases, such as cristobalite and mullite, formed.

The structure of the fired body is a complex conglomera-

tion of glassy, amorphous and crystalline material in varying stages of association and amount. Each phase contributes individual characteristics which complement each other to provide the properties of the total mass. Control of these properties is dependent upon adequate knowledge of the character and amount of the various phases present in the fired body. Previous methods for determination of quantitative data concerning the various phases have not been satisfactory. The complexities of the structures to be studied and limitations as to accuracy of methods employed are factors contributing to the present insufficient knowledge of the type and quantity of the various phases. The need for much fundamental work on the fired structure of whiteware bodies is evident.

The purpose of this investigation is to study the fundamental characteristics of the crystalline phases in vitrified whiteware bodies of the feldspathic type. A consideration of the methods available for the determination of the type and amount of the crystalline phase discloses that the two principal techniques are (1) a study of the microstructure by means of the petrographic microscope, and (2) interpretation of X-ray powder diffraction data. The microscope method is used extensively despite several limitations as to accuracy and ability to detect mullite and cristobalite crystals which frequently occur in submicroscopic size. The X-ray powder diffraction technique is used considerably for qualitative studies but has been used only in a limited degree for quantitative determinations. The principal limitations to greater use of this technique are the time and expense involved. This investigation is carried out with the aid of a Geiger-counter X-ray spectrometer which requires only one-tenth of the time for previous powder diffraction techniques. The rapidity and accuracy of the spectrometer technique are coincident with the requirements for industrial control methods.

The body compositions were organized to provide a fundamental study of Florida clay, Keystone feldspar and Ottawa

flint in one-, two-, and three-component blending combinations. A raw batch of each body was weighed, and then ground in a ball mill for 8 hours. The milled body was dried at 250°F. and reground in a porcelain mortar to pass an 80-mesh screen. The pulverized material was handpressed in a steel mold to form 1½ in. diameter pellets. The formed pellets were placed in specially prepared alundum crucibles for the firing operation. All bodies were fired in the same Globar furnace with similar heat treatment in regard to firing temperature of 1200° and 1400°C. and time of the soaking period of three and twelve hours. Specimens about ¾ in. square with a thickness of ½ in. were cut from the center portion of the fired pellets. A thin slice of material was cut from one surface of this specimen and used for preparation of thin sections and powdered specimens. The remaining solid portion was polished on the surface from which the slice of material had been previously removed to provide a finished specimen with ¾ by ¾ by ¼ in. dimensions. Quantitative determinations of the various crystalline phases were determined with X-ray spectrometer methods on polished and powdered samples of fired bodies. The amounts of the various crystalline phases as determined by the X-ray spectrometer were used to show the effect of composition, time and temperature of firing on the resulting structure of the various bodies. Transverse strength bars of several bodies were formed and fired in a manner analogous to the procedure used for the pellets. The results of physical tests on these specimens were correlated with the crystalline structure of the bodies as ascertained by quantitative X-ray studies with the Geiger-counter spectrometer.

The adaptability of the Geiger-counter X-ray spectrometer to investigations pertaining to reactions taking place in ceramic bodies at high temperatures has been shown. The advantages of the X-ray spectrometer technique over previous quantitative X-ray methods were greater resolution, greater accuracy (with certain techniques), elimination of

the photographic process and reduction to one-tenth of the time required for complete analysis. Two techniques were developed for the X-ray spectrometer method as follows: (1) powdered sample with reference material addition, (2) polished sample without a reference material addition. The powdered sample technique showed the greater accuracy and consistency of results. The polished solid technique was only slightly less accurate and showed potentialities as a control method for rapid determination of quantitative data of an approximate nature.

A fundamental study of the effects of composition, temperature and time of heat treatment on clay, feldspar and flint combinations was made with the X-ray spectrometer techniques. The following conclusions were drawn from such a study:

(1) Quartz, mullite, cristobalite and wollastonite were the only crystalline phases identified in the bodies studied.

(2) The most prevalent and readily ascertainable crystalline material in the test bodies studied was quartz. After a certain minimum temperature of 1200°C. had been exceeded, the length of the soaking period exerted the greatest influence on the conversion of quartz to cristobalite.

(3) Feldspar took only a small portion of quartz into solution at 1200°C., but the solubility increased rapidly with increase in temperature. Feldspar by itself reverted to a completely amorphous material with heat treatment to 1400°C. Percentages higher than 50 percent of feldspar tended to take considerable amounts of clay and flint into solution at the higher temperature of firing.

(4) A mullite crystalline phase was not observed in bodies which did not contain clay as a raw material. The presence of clay appeared necessary for the possibility of mullite formation. A body composed entirely of clay showed maximum theoretical mullite formation at even the lowest firing temperature of 1200°C. Addition of flint or feldspar retarded

the formation of the mullite phase considerably at 1200° C. temperatures and only slightly at the 1400° C. temperatures.

(5) Wollastonite was formed in clay-flint-feldspar bodies when 5 percent of whiting was added. Since cristobalite was not formed in these bodies, the wollastonite phase was formed probably as a result of direct crystallization rather than from devitrification changes during the cooling period.

(6) Summation of the various determined crystalline phases was used to obtain indirectly the amount of the amorphous phase for each body. The amount and behavior of the crystalline and amorphous phases for clay-flint-feldspar bodies was predictable from the combined picture of these materials in two-component arrangements.

(7) Thin section studies with the use of photomicrographs failed to provide a satisfactory knowledge of the microstructures of the fired bodies.

(8) Changes in modulus of rupture values with firing treatment could be satisfactorily explained with quantitative X-ray data concerning the crystalline and amorphous phases. Data obtained from physical tests and microscopic examinations did not satisfactorily explain such changes in strength values.

VITA

Milton Alfred Tuttle was born on September 27, 1920 in New Albany, Pennsylvania. He received his elementary and high school education under the public school system of Almond, New York. In 1937 he matriculated at the New York State College of Ceramics at Alfred, New York. He received the degree of Bachelor of Science in General Ceramic Technology and Engineering in June, 1941. An appointment to an Edward Orton, Jr. Ceramic Foundation Fellowship was granted him in order to work for a Master of Science degree. He completed the requirements for this degree in June 1942 and was granted the degree at that time. From June 1942 to October 1943 he was employed as a Research Assistant by the New York State Ceramic Experiment Station at Alfred, New York. He was inducted into the Army in October, 1943 and spent the next two years and four months in service, two years of which were spent in the E.T.O. Upon discharge from the service in January, 1946, he accepted an instructorship in Glass Technology at the New York State College of Ceramics. He matriculated at the University of Illinois in September, 1946 as the recipient of a fellowship in the Graduate College of that University.

He is a member of the American Ceramic Society, Keramos, Sigma Xi, Phi Psi Omega and the Spiked Shoe.

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